

Probing on growth and characterizations of SnFe_2O_4 epitaxial thin films on MgAl_2O_4 substrate

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Epitaxial tin ferrite (SnFe_2O_4) thin films were grown using KrF excimer (248 nm) pulsed laser deposition technique under different growth conditions. Highly epitaxial thin films were obtained at growth temperature of 650°C. The quality and epitaxial nature of the films were examined by X-ray diffraction technique. Furthermore, the phi-scans of the film and substrate exhibit fourfold symmetry, which indicates a cube-on-cube epitaxial growth of the film on MgAl_2O_4 substrate. Moreover, the magnetic force microscopy measurement shows domains with cluster-like structure, which is associated with ferromagnetic phase at room temperature. The coercive field and remnant magnetization of the films decrease with increase in temperature. These high quality ingenious magnetic films could be potentially used in data storage devices.

Keywords: epitaxial thin films, SnFe_2O_4 , pulse laser deposition, ferromagnetic, bandgap

INTRODUCTION

Recently, spinel ferrites with the general formula MFe_2O_4 (where $\text{M} = \text{Co}, \text{Mn}, \text{Mg}, \text{Sn}$, etc.) attract considerable research interest because of their wide applications in heterogeneous catalyst, sensors, transformers, magnetic recording, biomedical, etc. (Abdeen, 1998; Sedlář et al., 2000; Bao et al., 2007; Barcena et al., 2008; Xiang et al., 2010). The ferrites can be classified into different categories depending upon their cation distributions. Based on the cations distribution among the tetrahedral and octahedral sites of the coordinated oxygen, they can be either normal spinel $\text{M}^{2+}_{\text{Tetrahedral}}[\text{Fe}^{3+}\text{Fe}^{3+}]_{\text{Octahedral}}\text{O}_4$, or inverse spinel $\text{Fe}^{3+}_{\text{Tetrahedral}}[\text{M}^{2+}\text{Fe}^{3+}]_{\text{Octahedral}}\text{O}_4$ (Anantharaman et al., 1998).

Till date, most of the works on spinels have been reported on bulk in order to understand their magnetic behavior and correlate magnetic properties to their structural properties to improve their applications (Lüders et al., 2005). Epitaxial thin films of spinels have not drawn such a wide research attention despite of the fact that epitaxial films could modify the physical properties compared to the bulk material (Lüders et al., 2005). Epitaxial thin films of various ferrites have been grown using different techniques (Zimnol et al., 1997; Reisinger et al., 2003; Huang et al., 2007; Leung et al., 2008; Su et al., 2010). Among these techniques, pulsed laser deposition (PLD) is a very versatile and cost effective method which allows the stoichiometry transfer of multi-component materials from target to substrate (Green et al., 1995).

Pulsed laser deposition technique has been used for deposition of epitaxial thin films of magnesium ferrite on strontium titanate (Kim et al., 2010). The effect of post-annealing on the magnetic properties of epitaxial thin films of cobalt ferrite was studied (Axelsson et al., 2009). Nanostructured tin ferrites have been synthesized using different techniques (Liu et al., 2004; Liu and Li, 2005). It was also observed that the coercivity of the tin ferrite particles decreases with increase in the particle size (Liu et al.,

2004). Superparamagnetic behavior was observed for nanostructured tin ferrite (Liu and Li, 2005). PLD has been used to deposit (111) oriented epitaxial tin ferrite films on (0001) sapphire substrate (Gupta et al., 2011). In this communication, we report the epitaxial growth of tin ferrite films on (001) MgAl_2O_4 substrate using PLD technique. The quality and epitaxial nature of the films were evaluated by X-ray diffraction (XRD) diffraction technique. Magnetic domains with cluster-like structure were observed in the magnetic force microscopy (MFM) image of the film.

EXPERIMENTS

SnFe_2O_4 target for PLD was made using solid state reaction method. SnO_2 (99.9%, Alfa Aesar, USA) and Fe_2O_3 (99.5%, Alfa Aesar, USA) were used as received. The well-ground mixture was heated at 1200°C for 10 h. The powder mixture was cold pressed at $6 \times 10^6 \text{ N/m}^2$ load and sintered at 1400°C for 10 h. The films were deposited using KrF excimer PLD technique (Lambda Physik COMPex, $\lambda = 248 \text{ nm}$ and pulsed duration of 20 ns) at different substrate temperatures (550, 600, 650, and 690°C) under oxygen pressure of 0.1 mbar. The laser was operated at a pulse rate of 10 Hz, with energy of 300 mJ/pulse. The laser beam was focused onto a rotating target at a 45° angle of incidence. The target to substrate distance was 5 cm. Single crystal of (001) oriented MgAl_2O_4 was used as substrate. The substrate was ultrasonically cleaned in acetone and isopropanol for 10 min in each solvent.

The structural characterizations were performed using XRD. The XRD pattern of the films were recorded with Bruker AXS X-ray diffractometer using the 2θ - θ scan, rocking curve, and phi-scan with $\text{CuK}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) radiation which operated at 40 kV and 40 mA. The XRD measurements were performed using 0.1 mm aperture of the slits. The instrument broadening was corrected using LaB_6 as an instrumental broadening standard. MFM imaging was performed under ambient conditions using a Digital

Instruments (Veeco) Dimension-3100 unit with Nanoscope® III controller, operated in tapping mode. Magnetic measurements were performed on Quantum Design vibrating sample magnetometer (VSM). The optical transmittance measurements were made using UV–visible spectrophotometer (Ocean Optics HR4000).

RESULTS AND DISCUSSION

The epitaxial nature of the films was investigated by XRD technique. The different scans such as θ – 2θ , rocking (ω) curve, and ϕ (ϕ)-scans were used to study the quality and epitaxy of the films on (001) oriented MgAl_2O_4 substrate. Gupta and Yakuphanoglu (2011) and Gupta et al. (2011) have used sapphire and SrTiO_3 as substrate for epitaxial growth of SnFe_2O_4 . In the present study, MgAl_2O_4 was chosen as substrate since both film and substrate have cubic crystal structure with small lattice mismatch ($\sim 3.8\%$). All the films grown at different temperatures showed preferred orientation along (002) direction. **Figure 1** shows the θ – 2θ and rocking curve for (002) peak for the film grown at 650°C . It is seen in the XRD pattern that only one peak oriented along (002) direction is observed, indicating the epitaxial nature of the film along (002) direction. The epitaxial nature of the film is due to the close lattice parameters of film and substrate as both SnFe_2O_4 (face-centered cubic, $a = 0.842\text{ nm}$) and MgAl_2O_4 (cubic, $a = 0.808\text{ nm}$) exhibit cubic symmetry (space-group $\text{Fd}\bar{3}\text{m}$). The full width at half maximum (FWHM) of (002) peak was estimated using the rocking curve. The FWHM was calculated to be 0.42° , 0.42° , 0.39° , and 0.44° for the films grown at 550 , 600 , 650 , and 690°C , respectively. The lowest FWHM was observed for film grown at 650°C , indicating highly quality of the film. The FWHM was for SnFe_2O_4 film grown on SrTiO_3 substrate was reported to be 0.96° , 0.94° , 0.56° , and 0.96° for the films grown at 550 , 600 , 650 , and 690°C , respectively (Gupta and Yakuphanoglu, 2011). As observed, the FWHM for the SnFe_2O_4 films grown on MgAl_2O_4 are better than that on SrTiO_3 , which is due to the close lattice match of SnFe_2O_4 and MgAl_2O_4 . Although the lattice mismatch between the substrate and films is about 3.8% , the film shows strain of about 1.4% . We consider this high quality film for further characterizations. The ϕ (ϕ)-scan of the film and substrate was recorded using (311) reflection plane ($2\theta = 34.28$ and $\psi = 25.24$) and is shown in **Figure 2**. The ϕ -scan of the film and substrate revealed fourfold symmetry for both. The ϕ -scan shows a cube-on-cube epitaxial growth of SnFe_2O_4 on MgAl_2O_4 substrate.

Figure 3 shows the MFM image of the film recorded in the demagnetized state. The presence of magnetic domain due to grains of SnFe_2O_4 is quite evident in the MFM image. The grain size of the SnFe_2O_4 films was estimated to be 22 nm using (002) peak of XRD pattern (Gupta et al., 2011). The size of the magnetic domain was observed to be about 200 nm , indicating that about 10 grains make a domain. As seen in **Figure 3**, the magnetic image consists of domains with cluster-like structure where the magnetization is confined up and down with light and dark color, respectively.

The optical properties such as transparency and optical bandgap of the epitaxially grown tin ferrite were studied. **Figure 4** shows the optical transmittance spectra of the film. The optical

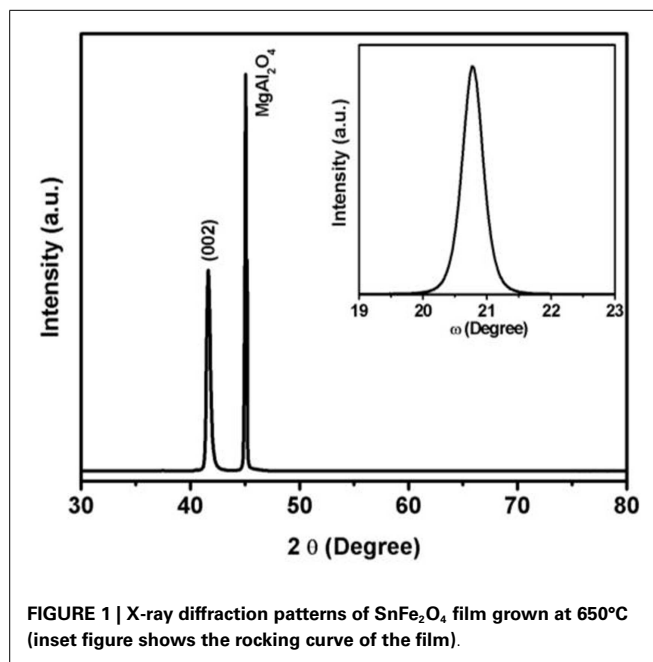


FIGURE 1 | X-ray diffraction patterns of SnFe_2O_4 film grown at 650°C (inset figure shows the rocking curve of the film).

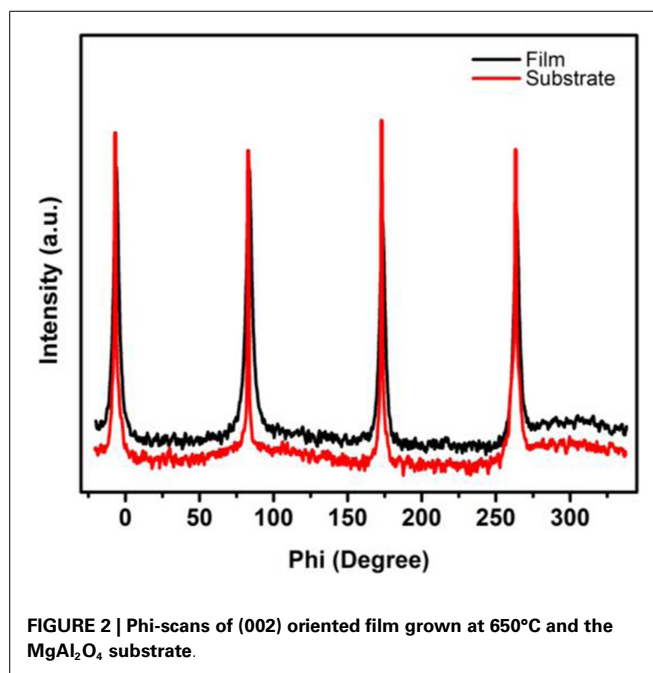


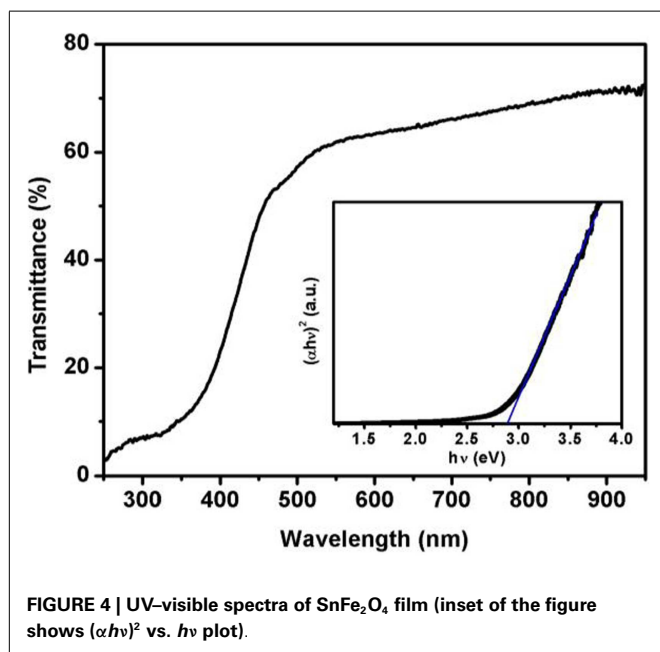
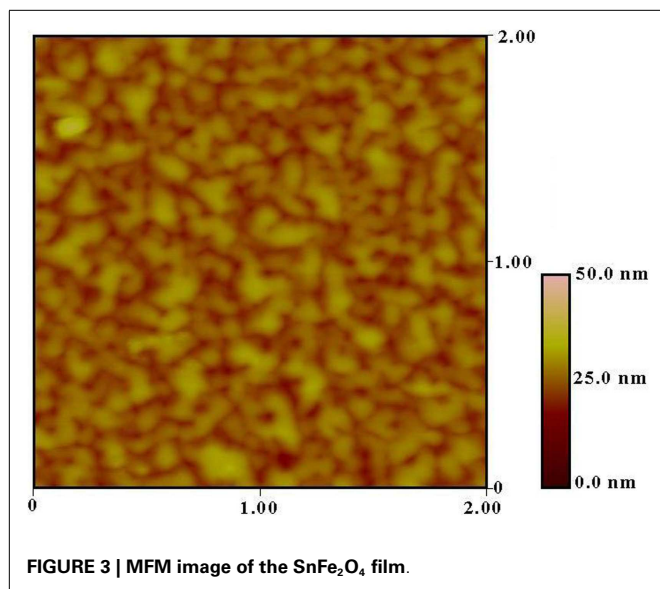
FIGURE 2 | ϕ -scans of (002) oriented film grown at 650°C and the MgAl_2O_4 substrate.

bandgap of the film was calculated from absorption coefficient and photon energy. The absorption coefficient (α) of the film was calculated using the following expression (Gupta et al., 2009)

$$\alpha = \ln \left(\frac{1}{T} \right) / d \quad (1)$$

where T is transmittance and d is film thickness. The optical bandgap of the films was calculated using the following equation (Dolia et al., 2006)

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$



where A and E_g are constant and optical bandgap, respectively. The E_g can be determined by extrapolations of the linear regions of the plots to zero absorption. Inset of **Figure 3** shows $(\alpha h\nu)^2$ vs. $h\nu$ plot for the film. The bandgap of the film was calculated to be 2.8 eV. A bandgap of 2.7 eV is observed for tin ferrite film grown on sapphire substrate (Gupta et al., 2011). Dolia et al. (2006) have observed a bandgap of 2.5 eV for nickel ferrite film, whereas the bandgap of 2.7 eV was reported for zinc ferrite film (Wu et al., 2001).

The magnetic properties of the film were studied under different conditions. **Figure 5** shows the variation of magnetization with temperature (M vs. T). As seen in **Figure 5**, the effect of temperature on magnetization was studied in zero-field-cooled (ZFC)

and field-cooled (FC) process under different applied magnetic fields. For the ZFC measurements, the film was cooled from high temperature to 10 K without applying any external magnetic field. After cooling to 10 K, an external magnetic field was applied and the magnetization of the film was recorded during the heating. For FC measurements, the magnetization is recorded while cooling the sample under an applied external magnetic field. As seen in **Figure 5**, during ZFC measurements the magnetization of the film increases with temperature up to ~ 275 K and then decreases with further increase in temperature. The nature of ZFC and FC curves is very similar but the magnitude of magnetization for FC curves is high. Similar results were observed for M vs. T process under high magnetic field. Furthermore, it should be noted that there is a distinct irreversibility between the ZFC and FC magnetization curves. This irreversibility persists up to high temperature of 375 K. Similar nature in M vs. T has been observed for the SnFe₂O₄ films grown on SrTiO₃ and sapphire substrate (Gupta and Yakuphanoglu, 2011; Gupta et al., 2011). The magnetization at 10 K in FC measurement was observed to be 12.9, 14.2 and 67.6 emu/cm³ for the SnFe₂O₄ film grown on MgAl₂O₄, SrTiO₃, and sapphire substrate, respectively. Although the maximum magnetization was observed on sapphire substrate, the difference in the values of magnetization measured during ZFC and FC at 10 K was almost constant (~ 10 emu/cm³) for the SnFe₂O₄ films on MgAl₂O₄, SrTiO₃, and sapphire substrate. The different values of magnetization for SnFe₂O₄ films on different substrates could be due to strain introduced by lattice mismatch of film and MgAl₂O₄, SrTiO₃, and sapphire substrates (Belenky et al., 2005). The lattice mismatch between SnFe₂O₄ and MgAl₂O₄, SrTiO₃, and sapphire was estimated to be 3.8, 7.3, and 8.4%, respectively. The strain introduced by lattice mismatch is an important parameter contributing to magnetic properties such as Curie temperature, coercivity, saturation magnetization, and anisotropy (Rao et al., 1998).

Figure 6 shows the variation of magnetization with applied magnetic field (M vs. H) at different temperatures. The M vs. H plots were measured at 10 and 300 K. The open hysteresis loop near origin at room temperature confirms the ferromagnetic nature of the film. It is observed that the coercive field and remnant magnetization of the film decrease with increase in the temperature. The coercive field of 4575 and 431 Oe is observed at 10 and 300 K, respectively. On the other hand, the value of remnant magnetization of 25.2 emu/cm³ and 8.3 emu/cm³ is observed at 10 and 300 K, respectively. The coercive field of 4861 and 1323 Oe was reported for SnFe₂O₄ film on sapphire substrate at 10 and 300 K, respectively (Gupta et al., 2011). On the other hand, the coercive field of 1853 and 801 Oe was observed for SnFe₂O₄ film on SrTiO₃ substrate at 10 and 300 K, respectively (Gupta and Yakuphanoglu, 2011). Again the difference in the remnant magnetization and coercive field for SnFe₂O₄ films on MgAl₂O₄, SrTiO₃, and sapphire substrates could be due to lattice mismatch between the film and substrates. The structural and magnetic characterizations of SnFe₂O₄ film on different substrates indicate that the properties of the film can be modified by using different substrates.

CONCLUSION

We have successfully demonstrated the deposition of epitaxial tin ferrite thin films on MgAl₂O₄ substrate using PLD technique. XRD

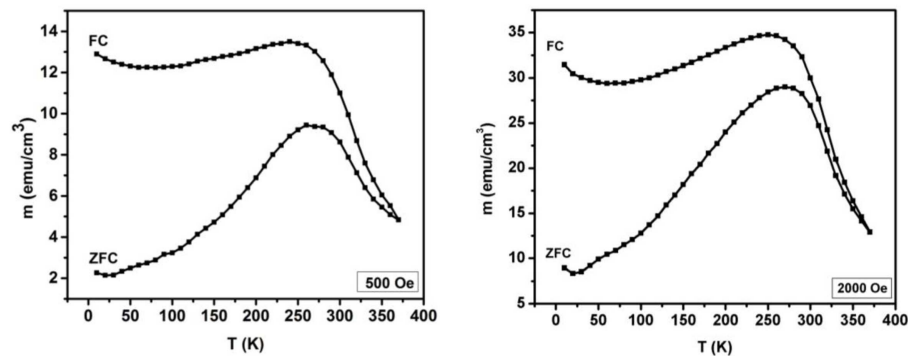


FIGURE 5 | M vs. T plots for SnFe_2O_4 film at different magnetic fields under FC and ZFC conditions.

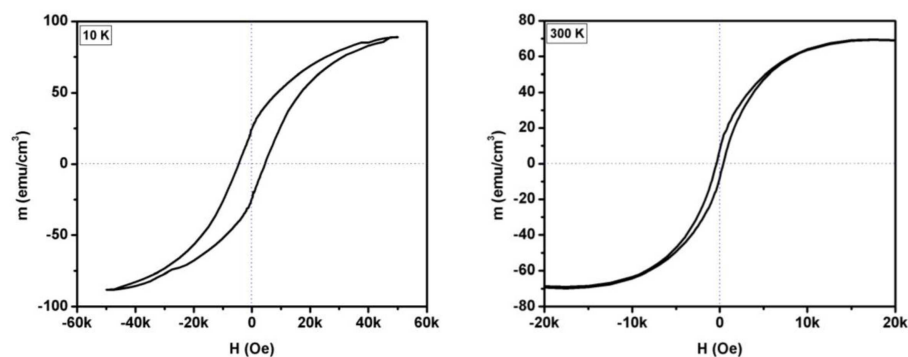


FIGURE 6 | M vs. H plot for SnFe_2O_4 film at different temperatures.

measurements confirm the epitaxial nature of the tin ferrite film. The ϕ -scan of the film and substrate shows fourfold symmetry, which evidenced the cube-on-cube epitaxial growth of tin ferrite on MgAl_2O_4 substrate. The optical bandgap of the film was observed to be 2.8 eV. Furthermore, the magnetic measurements exhibit the ferromagnetic nature of the film at room temperature. These epitaxial, transparent, and ferromagnetic films could be potentially used in the next generation data storage devices.

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